

# PATENT SPECIFICATION

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NO DRAWINGS.

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## COMPLETE SPECIFICATION.

### Improvements relating to the Formation of Metallic Coatings.

We, THE INTERNATIONAL NICKEL COMPANY (MOND) LIMITED, formerly known as The Mond Nickel Company Limited, a British Company, of Thames House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

It is often desired to apply a corrosion-resistant metal coating to a basis metal which is subject to corrosion, for example by atmospheric oxidation.

It is known to coat such a basis metal with a metal higher in the electrochemical series by immersing the basis metal in an aqueous solution of a salt of the coating metal. Such immersion plating methods are much simpler to carry out than electrolytic methods and are particularly applicable to the plating of inaccessible or discontinuous metal surfaces, for example the copper surfaces of printed circuits. However, only a thin coating can normally be obtained in this way, since as soon as the coating is a few atoms thick it effectively prevents the solution from coming into contact with the basis metal and coating ceases. Such a coating has little value since it is readily worn away and offers little protection to the basis metal against corrosion.

It is also known from U.S. Specification No. 2,532,283 to treat such a basis metal with an acid solution of a palladium salt to form a thin coating which is to serve as a foundation for a further coating formed by chemical reduction, the coating produced by following the directions in this United States

Specification being no more than 0.025 micron thick, and the further coating being of nickel and for example 50 microns thick.

According to this invention a porous adherent coating consisting essentially of a platinum metal is produced on the basis metal by chemical replacement by treatment with an acid solution of a salt of a platinum metal which dissolves more of the basis metal than is chemically replaced. The use of such a solution results in the formation of a porous coating which still allows the solution to reach the underlying metal through its pores, so that coating can continue so long as the metal is immersed in the solution. In the invention this treatment with the solution is continued until a thick coating is formed, that is to say, a coating far thicker than the palladium coating produced by the process described in U.S. Specification No. 2,532,283, and advantageously from 0.4 to 1.3 microns thick.

When the thick coating has been formed, the pores in it are sealed by a water-insoluble substance formed in the pores by chemical reaction to protect the basis metal from tarnishing and corrosion.

The acid that attacks the basis metal is conveniently the acid corresponding to the salt of the platinum metal, but other acids may be used. A solution containing a salt of the platinum metal and the corresponding free acid has in many cases the advantage that some or all of the metal is present in solution as complex ions, which favours the formation of an adherent coating.

Since the process according to the invention permits much thicker coatings to be formed than those obtainable by conventional

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chemical replacement, they are more resistant to wear, but owing to their porous nature, they do not fully protect the basis metal from corrosion. It is for this reason that, when the coating has reached the desired thickness the pores are sealed by a water-insoluble substance formed in the pores by chemical reaction, and preferably with a seal consisting of or containing precious metal. Sealing may be effected for example by precipitating in the pores a water-insoluble substance, such as an insoluble compound of the basis metal or of the platinum metal, or by immersing the coating in a sealing solution consisting of a conventional immersion plating solution of the kind that is used to form a non-porous metallic coating by chemical replacement or by chemical reduction. The purpose of the seal is to protect the basis metal from corrosion, and it does not add significantly to the thickness of the coating.

In the production of the porous coating on the basis metal it is necessary to control the various conditions quite closely. These conditions will vary for different basis metals, different platinum metals and different acids attacking the basis metal. The relative concentrations of the salt of the platinum metal and of the acid must be so adjusted that more basis metal is dissolved away than is replaced by the metal forming the coating. If the concentration of acid is too high, the basis metal will be dissolved away so quickly that no adherent coating is formed, while if the concentration is too low the chemical replacement reaction will predominate so that the porosity of the coating will be low and the formation of a thick layer will be inhibited.

Although the thickness of the coatings increases with time, it is important not to continue the coating process for too long, since this generally leads to exfoliation, i.e. flaking off of the coating, presumably because its adhesion to the basis metal has been impaired. A limit is thus set on the thickness of the coatings obtainable. It is found that the thickness at which exfoliation occurs depends on the concentration of the acid, and there may be an optimum concentration for the production of the thickest coatings. Thus in the plating of copper in a solution containing palladium in the presence of hydrochloric acid, optimum results were

obtained with a concentration of 250 ml./l. of concentrated (32%) hydrochloric acid, and variations of 5% on either side of this, i.e. concentrations of from 237.5 to 262.5 ml./l., resulted in a significant decrease in the maximum thickness (up to about 1.8 microns) obtainable prior to exfoliation taking place. The concentration of platinum metal in the solution does not appear to be as critical as that of the acid, since in the case mentioned varying the palladium content from 1 to 10 g./l. had no significant effect on the maximum thickness of coating obtainable. 5 g./l. was therefore chosen as a suitable operating concentration. However, it is important that this concentration should not be too high, since although the speed of plating may increase with increasing concentration of platinum metal, the metal deposit becomes dull and at higher concentrations still it becomes spongy, loose and non-adherent. The effect of temperature is to increase the rate of deposition of the metal coating, but no significant increase in the maximum thickness of coating obtainable is observed. When coating copper in the system palladium/hydrochloric acid room temperature is a convenient operating temperature.

Similar results are obtainable with other platinum-metal salt/acid systems, but one or more of the conditions may have to be altered for the best results in any particular case. Thus under the same conditions of acid and salt concentrations and at the same temperature, coatings from rhodium chloride and hydrochloric acid up to 0.8 microns thick were obtained. Coatings could not be satisfactorily deposited using platinum chloride solutions at similar acid and metal concentrations at room temperature, but by operating at 65° C. coatings up to 1.5 microns thick were readily obtained. In the case of ruthenium-containing solutions no satisfactory deposits were obtained from ruthenium chloride/hydrochloric acid solutions, but deposits up to 2.5 microns thick were obtained from solutions based on ammonium nitroso ruthenium chloride or ruthenium sulphamate in hydrochloric acid at 95° C., the concentrations of metal and acid again being the same as above. These results are summarised with respect to time and temperature in the following table:—

Platinum Metal in Solution	Temperature (°C.)	Time (Mins.)	Deposit Thickness in Microns
Rhodium .. ..	25	10	0.8
Ruthenium .. ..	95	30	2.5
Platinum .. ..	65	8	1.5
Palladium .. ..	25	8	1.3

Suitable salts for making up the working solutions containing 5 g./l. of a platinum metal in hydrochloric acid are palladous chloride, chloropalladous acid, sodium chloropalladate, ammonium chloropalladate, rhodium chloride, platinum chloride, and ammonium ruthenium nitroschloride.

Coatings can be applied by means of these solutions to other basis metals, including nickel silver, brass, and beryllium-copper, phosphor-bronze, and iron-nickel-cobalt-chromium alloys. On the other hand reactive metals such as iron, zinc, magnesium and aluminium cannot be satisfactorily plated with such solutions.

It is found that the platinum metal deposited from the coating solution tends to alloy with the basis metal, with the result that the coating consists essentially but not wholly of the platinum metal.

The sealing of the pores with a water-insoluble substance is most effectively carried out using the conventional immersion plating method to deposit a precious metal in the pores. These immersion plating solutions commonly contain a salt of the precious metal and may also contain a reducing agent, and are such that the whole of the metal dissolved is replaced by the precious metal. The precious metal, like the platinum metal in the porous coating, is deposited by chemical replacement of the basis metal, and must therefore be higher in the electrochemical series than the basis metal. It must, of course, also be resistant to corrosion. Although the precious metal may be the same as the platinum metal, we find that gold is particularly suitable for sealing the pores on copper and brass.

The method of sealing pores by a water-insoluble substance formed in them by precipitation is also useful when the coating is to be exposed to atmospheric corrosion. Conveniently the object being coated is removed from the plating solution and treated with a reagent that reacts with the solution remaining in the pores, to neutralise the substance that attacks the basis metal and precipitate an insoluble substance containing the platinum metal in the pores, but if desired the residual solution may first be replaced by another suitable solution before the precipitating reagent is applied.

The following are examples of solutions which can be used to seal by chemical reaction the pores in coatings obtained from solutions of salts of palladium, platinum, rhodium and ruthenium and prepared as described above:—

- (i) An ammonium hydroxide solution made by dissolving 1 part of ammonium hydroxide (specific gravity 0.880) in 2 parts of water;
- (ii) A gold immersion plating solution containing:—

Potassium gold cyanide 5 g./l.  
Ammonium citrate .. 20 g./l.  
Urea .. .. 25 g./l.

dissolved in water followed by addition of ammonia to bring the pH into the range 9—10;

- (iii) A solution containing hydrazine and ammonium hydroxide;
- (iv) A potassium iodide solution;
- (v) A 10% sodium hydroxide solution; and
- (vi) A 5% silver nitrate solution.

The process of this invention is particularly useful for the formation of coatings on non-precious basis metals. In particular the copper conducting elements of printed circuits may be coated by means of the process. Coatings consisting of a porous matrix derived from an acid solution of a platinum metal salt and having pores filled with gold are particularly suitable for the contact surfaces of sliding electrical contacts, especially those contacts used for low current applications, because the very desirable properties of both gold and the platinum metal are imparted thereto. Contacts coated in this way form an important feature of this invention. The basis metal of the contacts is preferably copper or brass.

Some examples will now be given.

#### EXAMPLE 1.

Twenty copper discs each having a total surface area of two square inches were polished and degreased, some by washing with acetone and degreasing cathodically and others by gentle wiping with a swab of cotton wool soaked in detergent solution. They were then immersed for 10 minutes in an aqueous solution containing 5 grams/litre (g./l.) of palladium as palladous chloride and 250 c.c./litre of concentrated hydrochloric acid (12N). The solution was kept at room temperature and was not agitated, as this was found to give deposits of poor adhesion. The discs were then rinsed by a quick dip in water and transferred as quickly as possible to a sealing bath containing 333 c.c./litre of aqueous ammonia (S.G. 0.880) and kept at room temperature. After 5 minutes the discs were removed, rinsed by thorough washing in water and dried with a clean, soft towel. They were then found to be uniformly covered with a bright adherent coating about 1.3 microns thick. The pores of the coating had been sealed with palladamine chloride.

#### EXAMPLE 2.

Twelve copper-plated brass discs, polished and degreased as described in Example 1, were immersed for 10 minutes at room temperature in an aqueous plating solution containing 5 g./l. of rhodium (as rhodium chloride) and 250 c.c./l. of concentrated hydrochloric acid, rinsed by dipping in water,

and at once transferred to a bath of aqueous ammonia as in the previous example. After drying the specimens were found to be uniformly coated with an adherent, bright coating about 0.8 microns thick, the pores of which had been sealed with rhodium hydroxide.

#### EXAMPLE 3.

A piece of sheet copper was cleaned, degreased, and immersed for 8 minutes at 65° C. in an aqueous solution containing 5 g./l. of platinum (as platinum chloride) and 250 c.c./l. of concentrated hydrochloric acid. It was then rinsed and immersed in a bath of aqueous ammonia in the same way as in Examples 1 and 2. This treatment produced a bright, uniform, adherent coating 1.5 microns thick, the pores of which had been sealed with ammonium chloroplatinate. In contrast to the first two examples, no coating could be obtained at room temperature.

#### EXAMPLE 4.

Six commercial printed circuits made of copper foil on laminated plastic were polished and degreased with detergent and then plated and sealed as in Example 1. Adherent bright deposits were obtained.

#### EXAMPLE 5.

Six commercial printed circuits made of copper foil on laminated plastic were polished and degreased with detergent as described above and then plated and sealed as in Example 2. Adherent bright coatings were obtained.

#### EXAMPLE 6.

A specimen sheet of copper was given a porous coating 1.3 microns thick by immersing it for 10 minutes at 15° C. without agitation, in an aqueous solution of 5 g./l. of palladium as palladium chloride and 250 c.c. of concentrated hydrochloric acid per litre. The specimen was then removed, rapidly rinsed in water, and then immersed for 5 minutes at 100° C. in a sealing bath consisting of:—

Potassium gold cyanide ..	5 g./l.
Ammonium citrate ..	20 g./l.
Urea ..	25 g./l.

dissolved in water followed by addition of ammonia to bring the pH into the range 9—10. As a result of this treatment the pores of the deposited layer were found to be sealed with gold and a film of gold was also formed on the surface of the specimen.

#### EXAMPLE 7.

Brass electrical contacts were carefully degreased and immersed successively in a coating solution and a gold sealing solution exactly as in the preceding example, except that the time and temperature of immersion in the palladium solution were 8 minutes and 25° C. respectively. When they were re-

moved from the sealing solution the contacts were found to be uniformly covered with a bright, adherent coating the pores of which were filled with gold and the surface of which was covered with a very thin continuous film of gold. The thickness of the coating was 1.3 microns, and the amount of gold in the coating was calculated to be such that it would have formed a continuous layer 0.05 microns thick on a non-porous surface.

#### EXAMPLE 8.

Transistor bases consisting of an alloy composed of 54% iron, 28% nickel and 18% cobalt were given a porous coating 1.3 microns thick by immersion for 10 minutes at 95° C. in a plating bath containing 5 g./l. of ruthenium as ammonium ruthenium nitroschloride and 250 c.c./litre of concentrated hydrochloric acid. They were then removed, rinsed with water, and coatings were sealed with gold by the procedure used in Examples 6 and 7. The resulting coatings were bright and adherent and consisted of a porous matrix the pores of which were filled with gold.

#### WHAT WE CLAIM IS:—

1. A process for producing an adherent metal coating on a basis metal by chemical replacement in which the basis metal is treated with an acid solution of a salt of a platinum metal which dissolves more of the basis metal than is chemically replaced, the treatment is continued until a thick coating is formed, and the pores in the coating are subsequently sealed by a water-insoluble substance formed in the pores by chemical reaction.

2. A process according to Claim 1 in which the pores of the coating are sealed by precipitating the water-insoluble substance.

3. A process according to Claim 1 or Claim 2 in which the acid in the solution is that corresponding to the salt of the platinum metal.

4. A process according to Claim 3 in which the solution is one of a platinum metal chloride and hydrochloric acid.

5. A process according to any one of the preceding claims in which the platinum metal salt used is a salt of palladium, platinum or rhodium.

6. A process according to any one of the preceding claims in which the pores of the coating are sealed by immersing the coating in a solution containing a salt of a metal higher in the electrochemical series than the basis metal to form a non-porous coating in the pores.

7. A process according to Claim 6 in which the pores of the coating are sealed with gold by immersion in a gold immersion plating solution.

8. A process according to Claim 7 in which

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- the surface of a printed circuit or electrical contact is provided with a coating consisting of a porous layer of platinum metal the pores of which are filled with gold and an additional surface film of gold.
9. A process according to Claim 8 in which the basis metal of the contact is copper or brass.
10. A process according to any one of the preceding claims in which the thickness of the porous coating is from 0.4 to 1.3 microns.
11. A process according to any one of Claims 1 to 3 in which the platinum metal forming the porous coating is ruthenium.
12. A process according to any one of Claims 1 to 10 in which the porous coating is formed on a copper surface by treatment with a solution containing from 1 to 10 g./l. of palladium or rhodium and from 237.5 to 262.5 ml./l. of 32% hydrochloric acid.
13. A process according to any one of Claims 1 to 10 in which the porous coating is formed on a copper surface by treatment with a solution containing from 1 to 10 g./l. of platinum and from 237.5 to 262.5 ml./l. of 32% hydrochloric acid at a temperature of 65° C.
14. A process according to any one of Claims 1 to 10 in which the porous coating is formed on a copper surface by treatment with a solution containing from 1 to 10 g./l. of ruthenium in the form of ammonium nitrose ruthenium chloride or ruthenium sulphamate and from 237.5 to 262.5 ml./l. of 32% hydrochloric acid at a temperature of 95° C.
15. A process according to Claim 1, substantially as herein described with reference to any one of Examples 1 to 8.
16. A basis metal coated by a process according to any of the preceding claims.
17. A printed circuit or electrical contact, the metal surface of which carries a coating consisting of a porous layer essentially of platinum metal, the pores of which are filled with gold, and an additional surface film of gold.
18. A printed circuit or electrical contact according to Claim 17 in which the basis metal of the contact is copper or brass.
19. A printed circuit or electrical contact according to Claim 17 or Claim 18 in which the porous layer is from 0.4 to 1.3 microns thick.
20. Copper or a copper-base alloy, the surface of which carries a coating consisting of a porous layer essentially of platinum metal, the pores of which are filled with gold, and an additional surface film of gold.
21. Copper or a copper-base alloy, the surface of which carries a coating consisting of a porous layer essentially of platinum, palladium, rhodium or ruthenium, the pores of which are filled with gold, and an additional surface film of gold.

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